Method for regenerating etching solutions containing iron for the use in etching or
pickling copper or copper alloys and an apparatus for carrying out said method

The present invention relates to a method for regenerating etching solutions contain-
ing iron for the use in etching or pickling copper or copper alloys and an apparatus
for carrying out said method.

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An important step in the treatment of surfaces made of copper or copper alloys is the
step of etching or pickling.

Especially in the production of printed circuit boards, a plurality of etching steps is
20   necessary. For example, in order to structure the conductor paths the printed circuit
board is coated with a photoresist, subsequently exposed and developed in such a
way that the copper areas being thus set free can be removed using suitable etching
methods. These etching methods are known for a long time in the field of producing
printed circuit boards. In "Handbuch der Leiterplattentechnik", Leuze Verlag, 1982, it
25   is described, for example, that etching solutions comprising $FeCl_3$ or $CuCl_2$ are used
because the corresponding etching rates are in the range of about 35 µm/min.

The chemical equation $Cu + 2\ FeCl_3 \rightarrow CuCl_2 + 2\ FeCl_2$ demonstrates that ferric
chloride oxidises Cu, which is subsequently dissolved in the form of Cu^{2+}.

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Generally, in these etching methods for structuring printed circuit boards, copper lay-
ers having a thickness of 15 to 40 µm or more are removed thereby increasing the
concentration of copper while consuming Fe(III) and, correspondingly, decreasing the
etching rate. In order to maintain a constant etching rate, a system is necessary
35   which continuously feeds fresh etching solution during the operation in order to re-
dose the concentration of Fe(III). However, this is only possible until a certain con-

5   centration of copper in the etching solution is reached. Therefore, a certain amount of the spent solution is permanently discharged to ensure a continuous operation. By means of this "feed-and-bleed" method, a constant ratio of the concentration of Fe(III) to the concentration of copper is established in the etching solution. Using $FeCl_3$, $CuCl_2$ is formed in the bath dissolving copper as well. Since two elements effective in

10   etching are present in the solution, the redox potential of the solution is measured to control the feeding and the feeding is adjusted to the local requirements. However, this results in a high consumption of the etching solution and the spent solution has to be collected outside the treatment chamber.

15   For the regeneration of the etching medium the copper has to be removed from the solution. Because of the high concentration of copper in the solution a method can suitably be used wherein copper is electrolytically deposited on a cathode. Thereby, chlorine gas is formed in turn at the anode leading to strict environmental and secu- rity restrictions. Furthermore, due to the high concentration of copper, a very high

20   current density is necessary to remove a sufficient amount of copper from the solu- tion. Therefore, the etching solutions are recycled on industrial scale because a local application at the production site for printed circuit boards is thus not economic. Addi- tionally, the $Fe(II)Cl_2$ being present has to be further re-oxidised to $Fe(III)Cl_3$. This is carried out under significant technical efforts by adding chlorine gas to the spent

25   etching solution, thereby forming $FeCl_3$.

Besides the removal of complete copper layers also methods being directed to the treatment of surfaces are applied in the production of printed circuit boards. Thereby, only a few micrometers are removed from the copper surface to prepare the copper

30   surface for the consecutive process in an ideal way. These solutions are mostly re- ferred to as microetching solutions.

Also for cleaning the material to be treated before the metallization a so-called etch- ing cleaner is normally used. Oxidative etching media are also employed in demetal-

35   lizing Cu and its alloys in various process steps. However, the etching rate of the methods described above is too high for this purpose. Furthermore, they are highly

5   corrosive resulting in a direct oxidation of the surface treated in the presence of at-
mospheric oxygen.

Thus, other etching media having an etching rate of about 1 µm/min are used for
treating surfaces. The most commonly used media are, for example, sodium persul-
10   fate (NaPS), caroate (KSO$_5$) or other persulfates in acids such as sulphuric acid,
phosphoric acid or methane sulfonic acid (MSA) and combinations thereof as well as
H$_2$O$_2$/H$_2$SO$_4$.

Due to the current requirements in the field of printed circuit boards concerning high
15   frequencies and the related control of impedance there is an increased search for
novel methods ensuring an economic production at the same or at a higher quality
level. Thereby, also processes enabling a sequential build-up (SBU) of a multi-layer
circuit board are examined. The use of microetching will be increased thereby. In or-
der to keep the costs low and, if necessary, to satisfy environmental restrictions, it is
20   necessary to provide suitable recycling systems to minimize the formation of waste
water.

Etching media consisting of H$_2$O$_2$ and acids exhibit the problem of a limited operating
life because the concentration of Cu increases and H$_2$O$_2$ is consumed by reduction.
25   On the one hand, the copper can be recycled by freezing-out, on the other hand,
copper sulfate that has to be further treated requiring an increased energy demand is
obtained. A method for regenerating H$_2$O$_2$/H$_2$SO$_4$ by cristallization is disclosed, for
example, in US 4,880,495.

30   Etching solutions based on NaPS are normally discarded at that time, when a critical
copper concentration has been reached. Leading to an increased mass treatment of
waste water.

If etching media containing iron such as FeSO$_4$/Fe$_2$(SO$_4$)$_3$ or Fe(NH$_4$)$_2$(SO$_4$)$_2$ or FeCl$_3$
35   are used, the etching rate is significantly impacted by the concentration of Fe(III).
However, Fe(III) is reduced to Fe(II), when the material to be treated having a copper

5   coating, is pre-treated or etched and Cu(II) is dissolved. Normally, the etching solu-
     tion is discarded at that time, when a specific concentration of Cu has been reached,
     and has to be freshly prepared.

     Several methods for regenerating etching solutions containing iron using an elec-
10   trolysis cell have already been suggested:

     US 4,265,722 describes a method wherein copper from an etching solution is trans-
     ferred into an electrolysis cell separated from the treatment chamber in order to re-
     enrich the oxidising agent and to deposit copper on the cathode. However, it is
15   pointed that using $FeCl_3$ is not suitable because chlorine gas is formed at the anode
     which can be avoided by keeping the ratio of Cu(I) and Cu(II) within narrow limits.
     Furthermore, very high current densities are necessary and Cu is deposited in form
     of a sludge. Moreover, $CuCl_2$ and $FeCl_3$ are highly aggressive towards conventional
     materials a treatment chamber is made up off. Therefore, the use of etching solutions
20   free of Cl ions is suggested. $Fe_2(SO_4)_3$ is used therefor and also iron oxide, iron car-
     bonate and iron ammonium sulfate are mentioned. Thus, only oxygen is developed at
     the anode which is released to the environment. The development of oxygen can
     also be inhibited by using low current densities. However, to increase the etching rate
     electrically conductive graphite and activated carbon powders are admixed to the
25   solution which have been treated at high temperatures preliminarily in a complex
     way. These particles are charged at the anode and assist the chemical etching of
     copper electrochemically. The anode consists of graphite tube and is surrounded by
     a diaphragm or an ion exchange membrane. The etching solution flows through the
     interior of the anode where the oxidising agent is re-enriched. Simultaneously the
30   solution reaches the cathode region through pores in the graphite tube where copper
     is subsequently deposited at the cathode.

     In WO 00/26440 a method is described, wherein a sulphuric iron solution for pickling
     copper and copper alloys is treated with or without peroxodisulfate after pickling in an
35   electrolysis cell separated from the treatment cells and is subsequently lead back into
     the pickling bath.

5   Therein, the dissolved copper is cathodically deposited in the electrolysis cell and
       Fe(II) is anodically re-oxidised to Fe(III). However, in this method a strict separation
       of the solution in the catholyte and in the anolyte is required, because otherwise
       Fe(III) formed at the anode is electrochemically reduced to Fe(II) at the cathode.
10   Moreover, the system can only be operated using low current densities to avoid the
       development of O_2 which is released to the environment reducing the oxidative etch-
       ing effect of the medium. Thus, several cells of that kind are required for a fixed vol-
       ume. The separation of anolyte and catholyte is achieved by ion exchange mem-
       branes or porous diaphragms also in this case. Diaphragms or membranes have a
15   limited lifetime. Additionally, the electric resistance is significantly increased during
       the electrolysis leading to further expenses for rectifiers and electric power. The feed-
       ing of the regenerated pickling solution is a result of the redox potential required in
       the treatment chamber.

20   W. H. Parker describes in Metal Program, V. 89, No. 5, May 1966, 133-134 the re-
       generation of ferric sulfate etch baths. Therein, Fe^{2+} is oxidised to Fe^{3+} at the anode.
       A perm selective membrane is provided to avoid the migration of iron ions to the
       cathode at which they would be reduced.

25   The examples mentioned above describe a strict separation of the solution in the ca-
       tholyte and in the anolyte because Fe(III) formed at the anode is electrochemically
       reduced to Fe(II) at the cathode and the efficiency of the copper deposition is signifi-
       cantly reduced thereby. The example mentioned above also describe open circular
       systems from which inter alia the oxygen formed at the anode is released and is thus
30   no longer available for the equilibrium reaction.

       The object underlying the preset invention is to provide a method for regenerating
       etching solutions containing iron which can be carried out in a compact electrolysis
       cell without a complex separation between the anolytes and the catholytes by dia-
35   phragms or ion exchange membranes.

5   The subject of the present invention is a method for regenerating etching solutions containing iron for the use in etching or pickling copper or copper alloys comprising the following steps:

(i)   transferring the etching solution from the etching system into an electrolysis cell
10   being hermetically sealed or having an anode hood (8), the electrolysis cell comprising an inert anode (2), a cathode (1), means (3) for removing the electrolytically deposited copper from the cathode and means (4) for collecting the removed copper and for applying a potential thereto, wherein the electrolysis cell does not comprise an ion exchange membrane or a diaphragm,

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(ii)   electrolytically depositing the copper comprised in the etching solution at the cathode (1),

(iii) oxidising Fe(II) comprised in the etching solution to Fe(III) at the anode (2),
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(iv) removing the copper deposited at the cathode (1),

(v)   applying a potential to the removed copper to permit a re-dissolving of the copper and
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(vi) returning the etching solution being thus treated into the etching system.

Basically, any etching media containing iron can be regenerated using the method according to the present invention. Such etching solutions are known per se by the
30   person skilled in the art and are described, for example, in "Handbuch der Leiterplattentechnik", Leuze Verlag, 1982, in US 4,265,722, in WO 00/26440 and in EP 794 69.

For example, $FeCl_3$ is present in an iron(III) chloride etching medium in a concentra-
35   tion of 300 to 450 g/l and HCl in an amount of 100 ml/l (32%). With this etching medium an etching rate of up to 50 μm/min is achieved at a temperature of 20 to 55°C.

5   Fe(III) (such as $Fe_2(SO_4)_3$) in a concentration range of 1 to 60 g/l and H_2SO_4 in a concentration range of 60 to 250 g/l at a temperature of 20 to 55°C are most commonly used as an iron(III) sulfate etching medium achieving etching rates of 0.1 to 1.5 µm/min.

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Surfactants such as polyethyleneglycol or polypropyleneglycol are further added in most cases to achieve an improved wetting of the copper and, thus, to achieve a more uniform etching performance.

15   The method according to the present invention has the significant advantage that no complex separation using a diaphragm or an ion exchange membrane in the electrolysis cell has to be carried out.

Small anode surfaces are preferably used in the method according to the present
20   invention, which are smaller than the cathode surface, because the gas being developed at the anode assists the oxidation of Fe(II) to Fe(III), if the process is controlled in a suitable way. ·

The method according to the present invention enables to maintain a constant con-
25   centration of Fe(III) in the treatment cell and to make the etching solution free of copper resulting in the possibility to achieve a constant etching rate.

The present invention is further illustrated below with reference to Figure 1.

30   Figure 1 shows a schematic representation of an apparatus for carrying out the method according to the present invention.

Figure 2 shows a schematic representation of the etching rate as a function of the concentration of Fe(III).

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5   Figure 3 is the schematic representation of the graphs of the concentration of Fe(III) and Cu(II) as a function of the treated copper surface, respectively.

Figure 1 schematically illustrates the apparatus according to the present invention for the regeneration of etching solutions containing iron. It comprises a separate, her-

10   metically sealed electrolysis cell having a cathode (1) and an inert anode (2), means (3) for removing copper electrolytically deposited at the cathode, means (4) for collecting the removed copper and applying a potential to the removed copper, an inlet (5) provided in the lower part of the electrolysis cell between the cathode (1) and the means (4) for collecting the removed copper and for applying a potential to the

15   removed copper and an outlet (6).

The anode (2) preferably consists of a mixed titanium oxide or is coated with platinum.

20   The cathode (1) is provided with a means (3) for removing the electrolytically deposited copper. For example, the cathode can be in the form of a rotating electrode provided with a stripping plate.

Thus, the copper deposited at the cathode can be removed and collected by suitable

25   measures. In this connection, the electrolysis cell comprises means (4) for collecting the copper stripped off the cathode such as a collecting hopper provided under the cathode, whereby an electric potential has to be applicable to the collecting means. The means (4) can be, for example, an electrically conducting collecting hopper or a conducting collecting tray.

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An essential feature of the method according to the present invention is that the etching solution to be regenerated contacts the cathode of the electrolysis cell first: Accordingly, an inlet (5) is provided in the lower part of the electrolysis cell between the cathode and the collecting means (4). The copper comprised in the etching solution

35   is thereby deposited at the cathode, while Fe(II) comprised in the solution is oxidised to Fe(III) at the inert anode. Thereby, the copper is removed from the etching solution

5   and Fe(III) ions are added thereto. The thus regenerated etching solution is returned to the etching system via an outlet (6).

The copper deposited at the cathode is collected in a collecting means (4) and can be discharged from the electrolysis cell via appropriate valves (7). A suitable potential
10 is applied to the copper via the conducting collecting hopper or the conducting collecting tray to avoid re-dissolving of the copper. The potential should be higher than 0.35 V to avoid re-dissolving.

The flow of the etching solution to be regenerated through the electrosis cell can be
15 controlled by on-line measurement of the Fe(II)/Fe(III) concentration or by on-line measurement of the copper concentration.

The relevant methods for determining the concentrations such as photometric methods or potentiometric measurements are known per se to those skilled in the art and
20 are described, for example, in user manuals of Fa. Dr. Lange in the case of photometry and Fa. Metrohm for the use of potentiometric measurements, respectively.

As indicated above, the etching rate depends on the concentration of Fe(III). The experiments carried out in a volume of 560 l demonstrated that etching rates between
25 0.1 µm/min. and 0.4 µm/min can be achieved if the concentration of Fe(III) is adjusted between 1.3 g/l and 7.5 g/l as indicated in Figure 2.

Modern production sites predominantly use etching facilities enabling to move a flat material to be treated horizontally through the treatment liquid. The following expla-
30 nations correspondingly apply to vertical facilities. For the purpose of demonstrating the efficiency of the apparatus according to the present invention, a horizontally operated etching system is assumed that is able to move a flat material to be treated, such as a printed circuit board, at a speed of 2 m/min through said system. In this example, the volume of the etching solution is 560 litres.

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5   A copper surface of 120 m^2 can be treated within one hour using said system
     whereby 1 μm is removed from this surface. This means that 560 l of etching solution
     receive about 1068 g of copper during this time. However, Fe(III) is oxidised to Fe(II),
     thereby impacting the etching rate.

10   Therefore, Fe(III) is produced by the apparatus according to the present invention to
     remain within the fixed process range, i.e., to achieve fixed values for the contents of
     Fe(III) and Cu(II).

     The treatment solution charged with copper and having a reduced concentration of
15   Fe(III) contacts the cathode first. Subsequently, two competitive processes occur
     there. On the one hand, copper is deposited at the cathode and, on the other hand,
     Fe(III) still present is reduced to Fe(II). Thereby, the efficiency of the copper deposi-
     tion, i.e., the ratio of the charge carrier provided and the amount of copper actually
     deposited, becomes less than 100%. The dominating processes and, consequently,
20   the control of the efficiency depends on the copper concentration in the solution, the
     approach flow of the solution to the cathode and the cathodic potential.

     The efficiency is within the range of 0 to 90%, depending on the cathodic potential
     and the cathodic current density, respectively. If the copper concentration differs too
25   much from the desired value, a low cathodic efficiency is achieved, resulting in an
     increasing copper concentration. In this case, Fe(III) is reduced at the cathode, lead-
     ing to a further increased content of Fe(II). When the copper concentration reaches
     the desired value, an equilibrium between the copper deposition and the cathodic
     reduction of Fe(III) establishes, resulting in a cathodic efficiency of 60 to 80%.

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     In the further course, the charged etching solution flows to the anode. If the copper
     concentration has not yet reached the desired value, the efficiency of the regenera-
     tion of the oxidising agent at the anode is already 100%, so that the constant concen-
     tration of Fe(III) accompanied by a constant etching performance is achieved. At low
35   potentials Fe(II) is oxidised to Fe(III) at the anode first. However, if there is not
     enough Fe(II) available at the anode, the development of a gas, such as oxygen, oc-

5   curs additionally in the case of using a solution free of chlorine. In order to avoid a
depletion of Fe(II) close to the anode, the volume flow continuously feeding Fe(II) has
to be increased.

If the solution contains too much Fe(II), the anodic current density has to be in-
10   creased to oxidise a sufficient amount of Fe(II) per time unit. This can result in an
increase in the anodic potential. However, the gas development (such as oxygen)
occurs at the anode at higher potentials.

It is an advantage of the apparatus according to the present invention that the plating
15   cell is within a closed system from which the gas (such as oxygen) cannot escape,
resulting in the dissolved gas supporting the oxidation of Fe(II) to Fe(III) and assisting
to adjust the concentration of Fe(II) to the desired value. For safety reasons, an over-
pressure valve is provided for the case of a too vigorous gas development, through
which an excess of oxygen can escape.
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For example, it follows from an efficiency of 80% that about 10 A are necessary to
remove about 9.5 g copper from the solution within one hour. Correspondingly,
1000 A are needed to deposit about 950 g copper. For depositing usually current
densities of 1 to 40 A/dm^2 are desired, preferably 10 to 25 A/dm^2, specifying the sur-
25   face of the cathode. The copper is removed from the cathode by a suitable device
and collected in a container under the cathode and under the inlet. Since the solution
containing Fe(III) ions is continuously fed from the treatment chamber, a re-dissolving
of the copper would be initiated. This is prevented by applying a potential of more
than 0.35 V to the collecting tray and, thus, to the copper.
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Figure 3 illustrates the graph of the concentrations of Fe(III) and Cu(II) in the etching
chamber as a function of the treated copper surface. Since the horizontal system
used herein was operated at a speed of 2 m/min (60 m^2/h cut-off), this representation
corresponds to a function of time. The apparatus according to the present invention
35   was operated at an anodic current density of 40 A/dm^2 and at a cathodic current den-
sity of 20 A/dm^2. The container for the treatment solution had a volume of 560 litres.

5   In Segment I of Figure 3 the cathodic current efficiency is not sufficient; in Segment II there is an equilibrium between the etched amount of copper and the cathodic depositing of copper; Segment III relates to the time after turning off the means for keeping the etching rate constant. It can be clearly seen that the pre-determined Fe(III) concentration of about 7.5 g/l is maintained throughout the operation time of

10   the regeneration unit. Moreover, it is evident how the content of Cu(II) increases and levels to about 15 g/l. In this equilibrium state the same amount of copper is etched from the material to be treated (etching rate 1 μm/min Cu, time 1 min) as is deposited in the regeneration unit. If the unit is turned off (at 30 m^2/ltr.), the content of Cu(II) increases again, while the concentration of Fe(III) decreases and, thus, the operation

15   range is left.

The electrolysis can be carried out using both direct current and pulsed current. Optionally, the current density can be selected at a level at which O_2 or Cl_2 are developed. Since O_2 and Cl_2 cannot escape from the closed system, it is available for the

20   oxidation of excess Fe(II).

Therefore, no diaphragms or ion exchange membranes are necessary and the efficiency of the re-oxidation is raised to a level, at which only a single cell having a small surface of the anode is necessary.

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Additionally to the significantly lengthened operation time of the etching solution, during which no new preparation becomes necessary, there is the further advantage that no two-step pre-cleaning is necessary, if an etching solution containing iron and having suitable wetting agents is used. Thereby, the required number of systems in one

30   site or the required number of treatment steps is reduced leading to a reduction of expenses.

List of numerals

35   1   cathode
     2   anode

5	3	means for removing electrolytically deposited copper
	4	means for applying a potential to the removed copper
	5	inlet
	6	outlet
	7	valve
10	8	anode hood